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HIGH-TEMPERATURE OXIDATION OF SILICIDES OF SOME RARE-EARTH METALS

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The relative stability of silicides of some rare-earth metals in air at high temperatures is investigated. It is found that scandium silicide is the most stable, and yttrium silicides are least stable.

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Rare-earth metals possess an important group of physico-chemical properties, which provide a promising outlook for their application in metallurgy and instrument engineering. Metal-like compounds of rare-earth metals with non-metals, in particular with silicon (Refs. 1, 2), which are stable in air up to relatively high temperatures, are of particular importance.

Information on the sintering resistance of the silicides of rare-earth metals is at present very limited. Thus, in (Ref. 3) it is reported that the disilicide of lanthanum oxidizes at 1300°C at a rapid rate, forming a gray low-density oxide layer which adheres very poorly to the surface of a specimen which has been oxidized. The oxidation of disilicide of dysprosium in immobile air at 1000°C for 782 hours showed that after the experiment the specimen was practically as hard as before, and preserved its silvery luster (Ref. 4).

In the present work an investigation was made of the relative stability of the silicides of some rare-earth metals in air at high temperatures.

Experimental Part

The investigation of relative stability of silicides of scandium, yttrium, lanthanum, and cerium was conducted on compact specimens using a technique described in (Ref. 5). Silicide samples, containing 99.9% of the principal component, were prepared by pressing the powder, and subsequently caking in high vacuum. A change in the weight of a sample, referred to unit area, was taken as a measure of the degree of oxidation. When investigating the kinetics of the oxidation, the samples were heated in a tubular oven in air. The experiments were conducted in the temperature range 300-1100°C, every 100 degrees, with the holding time from 3 to 10 hours and with weighing every 0.5 hour. The total duration of oxidation for every given temperature was determined by the character of the curve showing the gain in weight of a sample.

The oxidation of the lower scandium silicide (Table 1), having the maximum content of the metal, becomes significant above 900°C. Up to this temperature, the weight of a sample barely changes. A relatively solid, thin, stable oxide layer which is formed at 300°C obstructs further oxidation of silicide when the temperature is increased. This is indicated by the character of the isotherms for the gain in weight in the temperature range 400-900°C. On the basis of the established oxidation laws, one may assume that in the temperature range

* Numbers in the margin indicate pagination in the original foreign text.

TABLE 1

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KINETIC EQUATIONS FOR THE OXIDATION OF SILICIDES OF CERTAIN
RARE-EARTH METALS

Silicide	t, °C	Oxidation Law
Sc ₃ Si ₈	300	$y = 5,44 \lg \tau + 6,06$
	400	$y = 1,36 \tau$
	500	$y = 5,44 \lg \tau + 1,29$
	600	$y = 30,5 \lg \tau + 0,93$
	700	$y^{1,34} = 68,87 \tau$
	800	$y = 3,52 \lg \tau + 6,62$
	900	$y = 22,85 \lg \tau + 21,64$ (1)
	1000	$y = 35,2 \tau$ (0-1,5 $\frac{y}{y_{ac}}$) $y = 667,2 \tau$ (1,5 $\frac{y}{y_{ac}} - \infty$)
ScSi	500	$y = 1,29 \tau$
	600	$y = 3,14 \tau$ (1)
	700	$y^{1,07} = 24,58 \tau$
	800	$y^{1,68} = 898 \tau$
	900	$140,8y^2 + 1210,4y - 170424 \tau = 0$
	1000	$434,7y^2 + 14126,0y - 6140578 \tau = 0$
	1100	$y = 46,55 \tau$
Sc ₃ Si ₅	500	$y = 2,43 \lg \tau + 2,23$
	600	$y = 24,68 \lg \tau + 5,92$
	700	$y = 39,20 \lg \tau + 13,85$
	800	$y = 45,99 \tau$
YSi ₂	400	$y = 15,38 \lg \tau + 2,49$
	500	$y = 3,32 \lg \tau + 12,45$
	600	$y = 214,30 \lg \tau + 67,72$
La ₅ Si ₃	400	$y = 0,66 \lg \tau + 2,35$
	500	$y = 123,64 \lg \tau + 154,4 (0-3 \frac{y}{y_{ac}})$ (1)
	600	$y = 89,2 \tau$ (3 $\frac{y}{y_{ac}} - \infty$)
La ₃ Si ₂	400	$y = 4,02 \lg \tau + 3,05$ (1)
	500	$y = 5,68 \lg \tau + 5,60 (0-3 \frac{y}{y_{ac}})$ (1)
	500	$y = 100,36 \tau$ (3 $\frac{y}{y_{ac}} - \infty$)
La ₃ Si ₂	600	$y = 18,52 \tau$ (1)
LaSi	400	$y = 1,80 \tau$
	500	$y = 122,2 \lg \tau + 17,96$
	600	$y = 115 \tau$
LaSi ₂	300	$y = 9,80 \lg \tau + 30,97$
	400	$y = 6,77 \lg \tau + 27,96$
	500	$y = 20,59 \lg \tau + 39,96$
	600	$y = 32,22 \lg \tau + 15,55$
	700	$y = 31,03 \lg \tau + 9,0$
	800	$y = 50,09 \tau$
Ce ₅ Si ₃	300	$y = 26,75 \tau$
	400	$y = 265,31 \tau$
Ce ₃ Si ₂	300	$y = 37,23 \tau$ (0-1 $\frac{y}{y_{ac}}$) (1)
	300	$y = 99,52 \tau$ (1 $\frac{y}{y_{ac}} - \infty$)
CeSi	300	$y = 70,13 \tau$ (1)
CeSi ₂	300	$y = 4,55 \lg \tau + 11,58$
	400	$y = 40,5 \lg \tau + 29,00$
	500	$y = 119,3 \lg \tau + 45,29$

(1) - Hour

400-900°C an oxide layer is formed whose growth is determined by the diffusion process. At 900°C the chemical mechanism of the oxidation process changes somewhat, regardless of the fact that at this temperature the growth of the oxide layer in general obeys the logarithmic law. At 900°C, however, the oxide layer still possesses protecting properties. Increasing the temperature to

1000°C leads to an essential change in the corrosion of the lower scandium silicide. In this case, the scaling obeys the linear law, i.e., it is determined by crystallochemical changes. The fact that the oxidation rate at 1000°C changes its value, and the isotherm has the form of a broken line, shows that at this temperature the condition for the solidity of the layer is disturbed, and the layer loses its protecting properties. At this temperature a porous powder which is dark-brown in color is formed on the surface of the sample.

The investigation of the stability of scandium monosilicide showed (Table 1) that this compound begins to oxidize at a higher temperature ($\sim 500^\circ\text{C}$) than does the lower scandium silicide. The growth of the oxide layer essentially also obeys the logarithmic or the parabolic law in the entire temperature range being investigated, i.e., it is determined by the process of diffusion. The temperatures 500 and 600°C are an exception. At these temperatures, a very thin layer is formed due to the crystallochemical changes on the surface of a sample.

The oxidation of the higher scandium silicide (Table 1) obeys essentially the logarithmic law. The compound begins to oxidize noticeably above 700°C , and already at 900°C the surface oxide layer loses its protecting properties, and the oxidation proceeds to the interior of a sample. Initially, this process is manifested by the appearance of noticeable cracks on the surface of the sample, and then by the scaling of portions of the oxide layer.

Monosilicide is the most stable in the scandium-silicon system. As already indicated, in a majority of cases the growth of the protecting oxide layer obeys the logarithmic law, which is observed for a relatively long period of time during which a sufficiently thick scale layer can be formed. This shows that only a specific scale layer is involved in the diffusion retardation of the process; this scale layer is located near the silicide, and its growth in time is proportional to the growth of the entire scale.

An inspection of the temperature dependence of the oxidation rate for scandium silicides (Table 2) points to the complexity of this process, which is to a large extent due to the participation of both components in the oxidation process. The growth of the oxide layer on the surface of scandium silicide samples is determined by the oxidation of the silicon and metal components. It is curious that the apparent activation energy in the oxidation of the higher scandium silicide does not change in the entire temperature range under investigation, i.e., from 500 to 900°C . This indicates that the oxidation of the higher scandium silicide is, apparently, determined by the diffusion of oxygen into the silicide lattice, with the formation of a compound constituting the base of the oxide layer. A change in temperature within the interval indicated, or an increase in the holding time, does not lead to any substantial changes in the chemical mechanism involved in the formation of the oxide layer.

The oxidation of monosilicide and the lower scandium silicide is accompanied by changes in the apparent activation energy when the temperature is raised. It is interesting to note that the value of the apparent activation energy for monosilicide in the interval $500\text{--}600^\circ\text{C}$, and for the lower scandium oxide in the interval $700\text{--}900^\circ\text{C}$, are practically equal to the activation energy for the

TABLE 2

VALUES OF THE ACTIVATION ENERGY, AND THE EQUATIONS SHOWING THE TEMPERATURE DEPENDENCE OF THE OXIDATION RATE OF SILICIDES OF SOME RARE-EARTH METALS

Silicide	Temperature interval, °C	Apparent Activation energy, kcal/mole	Temperature Dependence of the Rate Constant
Sc_5Si_3	600--700	1788	$\lg K = 0,68 - 767/T$
	700--900	5831	$\lg K = 2,34 - 5232/T$
	900--1000	29302	$\lg K = 7,75 - 12723/T$
ScSi	500--600	6652	$\lg K = 3,04 - 2874/T$
	600--700	15911	$\lg K = 6,22 - 6649/T$
	700--1100	27006	$\lg K = 9,74 - 11726/T$
Sc_3Si_5	500--900	7210	$\lg K = 3,39 - 3131/T$
YSi_2	400--600	6037	$\lg K = 3,72 - 26,21/T$
La_5Si_3	400--600	15921	$\lg K = 8,77 - 6913/T$
La_3Si_3	400--500	1313	$\lg K = 1,09 - 570/T$
	500--600	23301	$\lg K = 10,89 - 10118/T$
LaSi	400--600	10449	$\lg K = 5,78 - 4537/T$
LaSi_2	500--700	1940	$\lg K = 1,78 - 842/T$
	700--800	13396	$\lg K = 5,77 - 5816/T$
Ce_5Si_3	300--400	6576	$\lg K = 6,13 - 2855/T$
CeSi_2	400--600	8898	$\lg K = 4,98 - 3864/T$

higher scandium silicide. This is, apparently, due to the formation of an oxide layer having practically the same chemical content. In the temperature interval 900--1000°C, the apparent activation energy for the oxidation of the lower scandium oxide is approximately identical to that for the oxidation of monosilicide in the interval 700--1100°C. This also points to the similarity of the processes taking place on the surfaces of both silicides in the temperature intervals indicated.

By analogy with the corresponding research dealing with the high-temperature oxidation of metals, generalized in the monograph by V. I. Arkharov (Ref. 6) and in a number of other articles (Refs. 7, 8), one may assume that the changes in the activation energy for the oxidation process of the compounds discussed corresponds to the changes taking place in both silicides themselves and the scale layers adjoining them. This, apparently, points to the fact that reactive diffusion in the zone of the contact surface of the silicide and the scale is, in the course of a few hours, the factor limiting the rate of the entire oxidation process. The diffusion consists of an escape of ion-atoms of a metal or nonmetal from the crystalline lattice of silicide followed by diffusion through the scale layer. It also consists of the same stages for oxygen atoms moving in the opposite direction. A change in the reaction rate with time, in the compound and in the scale layer adjacent to it, points to the commensurability of the rates for these elementary processes. In this connection, it should be noted that a change in the activation energy for the process corresponds to the full completion of the corresponding reaction on the surface of a sample.

An investigation of the oxidation of yttrium disilicide (Tables 1, 2) shows that the growth of the oxide layer for this compound obeys the logarithmic law up to 700°C, after which the sample turns rapidly into a dark-brown porous mass and disintegrates. When the temperature is raised above 600°C, apparently, on the surface oxide layer tensions arise which lead to a disruption of its solidity -- in particular, the solidity of the "reaction layer" located near the silicide itself. In this case, the rate of the chemical reaction between silicide and the diffusing gas influences the value of the total oxidation rate.

An investigation of the high-temperature oxidation of lanthanum silicides (Table 1) made it possible to establish the temperature limits for the stability of these compounds. The oxidation of the lower silicides La_5Si_3 and La_3Si_2 is completely analogous. Both of these compounds are stable up to 500°C. The region of temperature stability of lanthanum monosilicide is displaced by 100 degrees, as compared with the lower ones. Disilicide is the most stable in the lanthanum-silicon system. Hardly any increase in weight up to 700°C is observed for this compound.

An investigation of the temperature dependence of the oxidation rate for lanthanum silicides (Table 2) gives an idea of the oxidation mechanism in these compounds. The value of the apparent activation energy for this process is almost the same for the silicide La_5Si_3 in the entire temperature range, and for La_3Si_2 in the temperature interval 600-700°C. This permits one to assume that in the temperature ranges indicated, the oxidation mechanism for both silicides is identical. In this process, compounds are formed which have an almost identical chemical content. For the oxidation of monosilicide in the entire temperature range, and for the oxidation of lanthanum disilicide in the interval 700-800°C, the apparent activation energy has a practically identical value for the two compounds. An investigation of the oxidation rate for lanthanum disilicide confirms the supposition expressed above that on the surface of a sample a dense, stable, solid layer is formed which up to 700°C obstructs the diffusion of all the components participating in the oxidation process. After that, the mechanism of the process itself is changed. In all probability, up to 700°C mainly the silicon component of the compound, which forms with the reagents in air a dense silicate layer, is oxidized. At higher temperatures, the protecting properties of this layer are disrupted, apparently, as a /2254 result of chemical instability of the compound being formed, and a process is initiated leading to the formation of a compound in which the metallic component predominantly participates.

At high temperatures cerium silicides are the most unstable. Only for a richer compound which contains the least metal in the system cerium-silicon have we succeeded in determining the apparent activation energies, the values of which differ only slightly for the two phases (6576 and 8898 kcal/mole).

Disilicide is the most stable among cerium silicides. Even at 600°C, its oxide layer possesses some protecting properties. Cerium monosilicide and Ce_3Si_2 are unstable even at 300°C.

On the basis of the above considerations, one may draw certain general conclusions as to the mechanism and kinetics of the oxidation of silicides of the rare-earth metals mentioned above. Oxidation at high temperatures is a complex process in which several elementary components participate; the interaction of these components changes substantially with the variation of temperature and duration. However, the formation of solid oxide layers in a sufficiently wide temperature interval is characteristic of almost all silicon-rich silicides. The fact that the activation energy at the temperatures corresponding to the formation of a dense oxide layer has practically the same value for all the disilicides under consideration makes it possible to draw the conclusion that silicon is the main component of this oxide layer. Since at present there are no data on the chemical analysis and the crystalline structure of the oxide layer, it is difficult to draw any authentic conclusions as to the mechanism of its formation.

With an increase in temperature and the metallic component in silicides, the apparent activation energy increases substantially by a factor of two or even four.

Conclusions

1. An investigation was made of high-temperature oxidation of silicides of scandium, yttrium, lanthanum, and cerium. At high temperatures in air, the most stable are scandium silicides, among which monosilicide possesses the greatest stability up to 1000°C. Yttrium silicides are the least stable.
2. The temperature dependence of the oxidation rate constant for all the silicide phases being investigated has been established. For a number of compounds, there is a change in the activation energy with a temperature change.
3. Hypothetical conclusions have been drawn as to the mechanism of the oxidation processes of the compounds indicated.
4. The oxidation process for silicides of rare-earth metals represents a complex process, passing through several stages, which is indicated by a change in the apparent activation energy with temperature.

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